

GEO-SEQ Project Quarterly Status and Cost Report December 1, 2001–February 28, 2002

Project Overview

The purpose of the GEO-SEQ Project is to establish a public-private R&D partnership that will:

- Lower the cost of geologic sequestration by: (1) developing innovative optimization methods for sequestration technologies with collateral economic benefits, such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coalbed methane production; and (2) understanding and optimizing trade-offs between CO₂ separation and capture costs, compression and transportation costs, and geologic sequestration alternatives.
- Lower the risk of geologic sequestration by: (1) providing the information needed to select sites for safe and effective sequestration, (2) increasing confidence in the effectiveness and safety of sequestration by identifying and demonstrating cost-effective monitoring technologies, and (3) improving performance-assessment methods to predict and verify that long-term sequestration practices are safe, effective, and do not introduce any unintended environmental impact.
- Decrease the time to implementation by: (1) pursuing early opportunities for pilot tests with our private sector partners and (2) gaining public acceptance.

In May 2000, a project kickoff meeting was held at Ernest Orlando Lawrence Berkeley National Laboratory (Berkeley Lab) to plan the technical work to be carried out starting with FY00 funding allocation. Since then, work was performed on four tasks: (A) development of sequestration co-optimization methods for EOR, depleted gas reservoirs, and brine formations; (B) evaluation and demonstration of monitoring technologies for verification, optimization, and safety; (C) enhancement and comparison of computer-simulation models for predicting, assessing, and optimizing geologic sequestration in brine, oil, and gas, and coalbed methane formations; and (D) improvement of the methodology and information available for capacity assessment of sequestration sites.

This Quarter's Highlights

- The GEO-SEQ Advisory Committee met on January 23–24, 2002, at Berkeley Lab. A summary of the meeting was prepared and sent to everyone associated with the Project.
- A three-dimensional model of a synthetic oil reservoir was developed. It captures geologic uncertainty, to allow the making of different realizations of the system's geology (Subtask A-1).
- The processing and interpretation of data from baseline field surveys carried out at the central Vacuum Field, New Mexico, was completed. A report with the initial results of this work has been prepared (Subtask B-2).

- Isotopic and chemical data on the Lost Hills gases indicate that the complex injection program used in this field did not result in a greater influx of CO₂ to the production wells. The results seem to indicate that the CO₂ may have had sufficient time to interact more extensively with the reservoir's water and/or hydrocarbons (Subtask B-3).
- Model comparison for two simple sets of numerical-simulation problems related to CO₂ sequestration in deep, unmineable coal seams has been completed (Subtask C-1).
- The proposed pilot CO₂ injection project in the Frio Formation to be performed near Houston, Texas, was selected by DOE (Subtask D).

Papers Submitted, Published or Presented During This Quarter

Doughty, C., Flow and transport modeling of CO₂ sequestration in brine-bearing formations, Presentation to the Berkeley Lab Earth Sciences Division Peer Review Panel, Berkeley, CA, February 12–13, 2002.

Hoversten, G.M., R. Gritto, J. Washbourne, and T. Daley, Fluid saturation and pressure prediction in a multi-component reservoir by combined seismic and electromagnetic imaging, Extended Abstract Submitted to the 2002 Annual SEG Meeting (Salt Lake City, October 6–11, 2002).

Law, D. H.-S., L.H.G. (Bert) van der Meer and W.D. (Bill) Gunter, 2001, Numerical-simulation comparison study for enhanced coalbed-methane recovery processes, Part I: Pure carbon dioxide injection, Paper SPE 75669, Accepted for Presentation at and Publication in the Proceedings of the SPE/CERI Gas Technology Symposium (GTS) 2002, Calgary, Alberta, Canada, April 30–May 2, 2002.

Oldenburg, C.M., and S.M. Benson, CO₂ injection for enhanced gas production and carbon sequestration, Soc. Petrol. Eng. SPE-74367, Paper Presented at the 2002 SPE International Petroleum Conference and Exhibition, Villahermosa, Mexico, February 10–12, 2002.

Pruess, K., C.M. Oldenburg, G.J. Moridis, and S.W. Webb, Vertical mixing of CO₂ and CH₄ with gravity effects, Paper Presented at the 2001 Fall Meeting of the American Geophysical Union, San Francisco, December 2001, EOS Trans. AGU, 82(47), Fall Meet. Suppl., Abstract H51A-0300, 2001, p. F485.

Oldenburg, C.M., and S.M. Benson, Feasibility of carbon sequestration with enhanced gas recovery (CSEGR), Abstract Submitted to GHGT-6 Conference, Kyoto, Japan, October, 2002.

Zhu, J., K. Jessen, A. R. Kavscek, and F.M. Orr Jr., Analytical solutions for coalbed methane displacement by gas injection, Paper Submitted to the Society of Petroleum Engineers and Presented at the SPE/DOE Thirteenth Symposium on Improved Oil Recovery, Tulsa, OK, April 13–17, 2002.

Seventeen technical talks on the various GEO-SEQ project tasks were presented during the January meeting of the GEO-SEQ Advisory Committee. In addition, the following 10 abstracts

were submitted to the Sixth International Conference on Greenhouse Gas Control Technologies (GHGT-6), Kyoto, Japan, October 1–4, 2002:

Benson, S.M. et al., The GEO-SEQ Project: A status report.

Doughty, C., S.M. Benson, and K. Pruess, Capacity investigation of brine-bearing sands for geologic sequestration of CO₂.

Hoversten, G.M., R. Gritto, T.M. Daley, E.L. Majer, and L.R. Myer, Crosswell seismic and electromagnetic monitoring of CO₂ sequestration.

Hovorka, S.D. and P.R. Knox, Frio Brine sequestration pilot in the Texas Gulf Coast.

Johnson, J.W. and J.J. Nitao, Reactive transport modeling of geologic CO₂ sequestration at Sleipner.

Law, D. H.-S., L.H.G. (Bert) van der Meer and W.D. (Bill) Gunter, Comparison of numerical simulators for greenhouse gas storage in coalbeds, Part II: Flue gas injection.

Myer, L.R., G.M. Hoversten, and C.A. Doughty, Sensitivity and cost of monitoring geologic sequestration using geophysics.

Newmark, R., A. Ramirez, and W. Daily, Monitoring carbon dioxide sequestration using electrical resistance tomography (ERT): a minimally invasive method.

Oldenburg, C.M., D. H.-S. Law, Y. Le-Gallo, and S.P. White, Mixing of CO₂ and CH₄ in gas reservoirs: Code comparison studies.

Pruess, K. et al., Code intercomparison builds confidence in numerical models for geologic disposal of CO₂.

Task Summaries

Task A: Develop Sequestration Co-Optimization Methods

Subtask A-1: Co-optimization of Carbon Sequestration, EOR, and EGR from Oil Reservoirs

Goals

To assess the possibilities for co-optimization of CO₂ sequestration and EOR, and to develop techniques for selecting the optimum gas composition for injection. Results will lay the groundwork necessary for rapidly evaluating the performance of candidate sequestration sites as well as monitoring the performance of CO₂ EOR.

Previous Main Achievements

- Screening criteria for selection of oil reservoirs that would co-optimize EOR and maximize CO₂ storage in a reservoir have been generated.
- An engineering approach to increase CO₂ storage during EOR was developed.

Accomplishments This Quarter

- Work was completed on developing a synthetic, 3-D model of an oil reservoir.

Progress This Quarter

The synthetic 3-D model of an oil reservoir is based upon an actual field. The reservoir model is stochastic such that various realizations of geology can be made and thereby capture geologic uncertainty. The model is consistent with input formats for the Eclipse and 3DSL oil reservoir simulators.

A postdoctoral researcher (Yuandong Wang) was identified and hired. He will be joining the Stanford group soon and will work on co-optimization.

Work Next Quarter

Now that the reservoir model is established, various reservoir development scenarios will be considered to better understand reservoir development techniques that maximize the simultaneous production of oil and storage of CO₂. We plan to examine and contrast:

1. Gravity drainage by injection into the top structure of a reservoir
2. Water-alternating-gas (wag) drive mode
3. Co₂ injection early in production life versus late in reservoir life
4. Co₂ injection following water flooding
5. Stripping of Co₂ from a mixture of Co₂ and N₂ that simulates an incompletely separated combustion gas

Subtask A-2: Feasibility Assessment of Carbon Sequestration with Enhanced Gas Recovery (CSEGR) in Depleted Gas Reservoirs

Goals

To assess the feasibility of injecting CO₂ into depleted natural gas reservoirs for sequestering carbon and enhancing methane (CH₄) recovery. Investigation will include assessments of (1) CO₂ and CH₄ flow and transport processes, (2) injection strategies that retard mixing, (3) novel approaches to inhibit mixing, and (4) identification of candidate sites for a pilot study.

Previous Main Achievements

- On the basis of numerical-simulation studies, the proof-of-concept of CO₂ storage with enhanced gas recovery (CSEGR) has been demonstrated.
- An engineering approach to increase CO₂ storage during EOR was developed.
- Initial feasibility was assessed through numerical simulation of CO₂ injection into a model system, based on the Rio Vista gas field in California.
- The numerical-simulation capability supporting this assessment is being improved through enhancement to the TOUGH2-EOS7C code.

Accomplishments This Quarter

- The results of the comparison between the Dusty Gas Model (DGM) and the Advective Diffusive Model (ADM) were presented at the Fall 2001 meeting of the American Geophysical Union.
- We initiated discussion with Scott Stevens of Advanced Resources International (ARI) on the possibility of his assisting the Berkeley Lab group in carrying out an economic-feasibility assessment for CSEGR.

Progress This Quarter

Karsten Pruess and Curt Oldenburg attended the Fall Meeting of the American Geophysical Union (San Francisco, California, December 10–14, 2001) and presented a poster on one-dimensional gravity-stable CO₂-CH₄ interdiffusion using the Advective Diffusive Model (ADM) and the Dusty Gas Model (DGM). It was concluded that the ADM and DGM agree well for all but the lowest-permeability cases. In further discussion with people at the conference, the dependence of Knudsen diffusion coefficients on permeability was considered. This dependence is being investigated.

Curt Oldenburg attended the Society of Petroleum Engineers' International Petroleum Conference and Exhibition in Mexico (IPCCEM), February 10–12, 2002, Villahermosa, Mexico, where he gave a presentation on CSEGR. The paper was very well received; many potentially important contacts were made. Curt is still following up with these contacts and trying to identify potential pilot study sites for a test CO₂ injection.

Berkeley Lab also initiated discussion with Scott Stevens (ARI) to help with an economic feasibility assessment of CSEGR. Scott will give a seminar at Berkeley on May 10, 2002. By that time, a subcontract might be in place for him to work with the Berkeley Lab group on the

economics of CSEGR. In addition, an abstract on CSEGR feasibility was submitted to the Kyoto, Japan conference in October.

Work Next Quarter

We will carry out simulation studies in support of the economic feasibility assessments of CSEGR. ARI will assist Berkeley Lab in these studies; Berkeley Lab will provide literature, data, and simulation results from Rio Vista for ARI's use.

In addition, we will continue investigations of the comparison of DGM and ADM to include variation in Knudsen diffusion coefficient as a function of permeability. Moreover, the search for potential CSEGR pilot site(s) will continue (with contacts developed at the SPE meeting in Villahermosa).

Subtask A-3: Evaluation of the Impact of CO₂ Aqueous Fluid and Reservoir Rock Interactions on the Geologic Sequestration of CO₂ with Special Emphasis on Economic Implications.

Goals

To evaluate the impact on geologic sequestration of injecting an impure CO₂ waste stream into the storage formation. By reducing the costs of the front-end processes, we could dramatically lower the overall costs of sequestration. One approach is to sequester less-pure CO₂ waste streams that are less expensive or require less energy to separate from flue gas.

Previous Main Achievements

- Potential reaction products have been determined, using reaction-progress chemical thermodynamic/ kinetic calculations, for typical sandstone and carbonate reservoirs into which an impure CO₂ waste stream is injected.

Accomplishments This Quarter

- Reactive-transport (open system) chemical kinetic simulations were planned using the reactive-transport simulator CRUNCH.
- Confirmatory reactive transport experiments were planned to lend credibility to the model calculations and simulations done to date and planned for the future.
- Presentations of FY01 accomplishments and FY02 plans were provided to the GEO-SEQ Advisory Committee during its annual program review held in January 2002.

Progress This Quarter

During this seventh quarter of work, we hoped to continue the process of evaluating the impact of waste stream CO₂, as well as contaminants (e.g., SO₂, NO₂ and H₂S), on injectivity and

sequestration performance. We planned to construct a series of simulations equivalent to those that occur along a 1-D flow path, using full-dissolution kinetics (including acid catalysis) for all the mineral phases present in the reservoir rock. The simulation can be visualized as following chemical reactions that take place through space and time along a single streamline. A rock composition and modal abundances appropriate for a feldspathic-sandstone reservoir containing clay and carbonate (with a Fe-bearing carbonate component) was used. Earlier work focused on closed-system simulations, while these new simulations add the effect of transport.

Because of a lack of funds, we could not accomplish the planned modeling work involving the reactive-transport simulations using CRUNCH (Steefel 2001). However, we were able to at least begin the process of planning the confirmatory reactive transport experiments that we outlined as part of our FY02 plans. Chemical/mineralogical conditions, including waste-stream contaminants, were designed to be analogous to the previously run reaction progress (closed-system) simulations, but with the additional consideration of flow added.

This modeling work was presented during the January 2002 meeting of the GEO-SEQ Advisory Committee. The committee strongly encouraged us to begin these experiments, as soon as possible, to lend credibility to the model calculations and simulations done to date and planned for the future. We completely agree with the committee that these experiments are crucial.

We also began defining sampling requirements for the newly approved Frio Brine Pilot Project (see Task D). We have contacted a manufacturer of a self-packing submersible pump to see if the design could be modified to provide useful aqueous and gas samples from the Frio wells.

Work Next Quarter

Now that FY02 funding has arrived, we will continue investigating the impact of other contaminants (SO_2 , H_2S , NO_2 , etc.) in the CO_2 waste stream. Our plan is to continue the process of accounting for the impact of fluid flow on sequestration by conducting open-system (reactive-transport) calculations analogous to the closed-system calculations made previously. We will also design and begin conducting confirmatory reactive-transport experiments using our unique plug-flow reactor. Descriptions of this apparatus will be provided in the next GEO-SEQ quarterly report.

Task B: Evaluate and Demonstrate Monitoring Technologies

Subtask B-1: Sensitivity Modeling and Optimization of Geophysical Monitoring Technologies

Goals

To (1) demonstrate methodologies for, and carry out an assessment of, the effectiveness of candidate geophysical monitoring techniques; (2) provide and demonstrate a methodology for designing an optimum monitoring system; and (3) provide and demonstrate methodologies for interpreting geophysical and reservoir data to obtain high-resolution reservoir images. The

Chevron CO₂ pilot at Lost Hills, California, is being used as an initial test case for developing these methodologies.

Previous Main Achievements

- A methodology for site-specific selection of monitoring technologies was established and demonstrated.

Accomplishments This Quarter

- Berkeley Lab demonstrated a methodology for jointly interpreting crosswell seismic and electromagnetic data, in conjunction with detailed constitutive relations between geophysical and reservoir parameters, to quantitatively predict changes in effective stress, gas saturation, and gas/oil ratio in a reservoir undergoing CO₂ flood.

Progress This Quarter

It was shown that by combining seismically derived changes in compressional and shear velocities with EM-derived changes in electrical conductivities, estimates of changes in effective pressure, water saturation, gas saturation (ΔS_g), and gas/oil ratio (ΔR_g) can be made in a complex reservoir containing oil, water, hydrocarbon gas, and introduced CO₂. The resulting predicted ΔS_g and ΔR_g are better correlated with logged unit boundaries than any other geophysical changes in parameters. The predicted ΔS_g and ΔR_g images indicate that a significant portion of the injected CO₂ is filling the upper portions of the section above the intended injection interval. These conclusions are validated by CO₂ injectivity measurements made in the 11-8WR well at Lost Hill. An extended abstract on this work was submitted to the organizers of the 2002 Annual SEG Meeting.

The calculated ΔR_g and ΔS_g generated from a set of geophysical parameter changes are depicted in Figure 1. The computations are based on differences calculated from reference values of effective pressure (P), reservoir porosity (ϕ), water saturation, S_w , and gas saturation, S_g . The sensitivity of the ΔR_g and ΔS_g predictions to the reference parameters has been studied and shows that the calculations are relatively insensitive to the reference ϕ and S_w values. The calculations are most sensitive to the reference pressure.

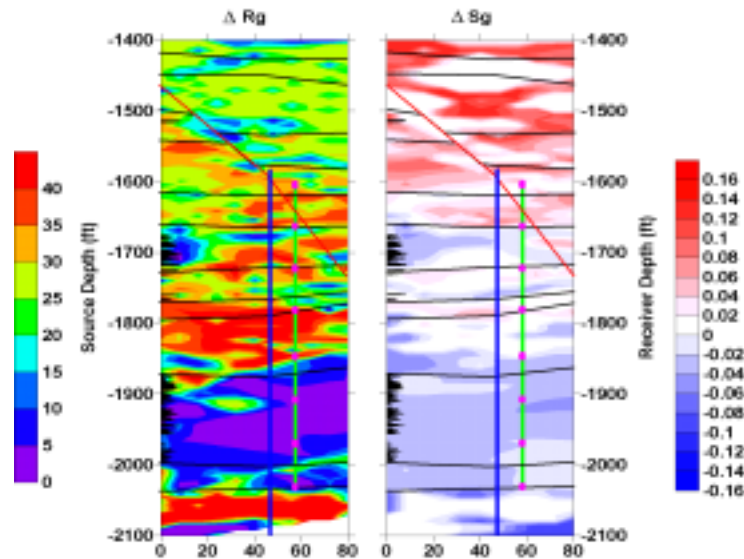


Figure 1. Predicted ΔR_g (left side) and ΔS_g (right side). Initial OB-C1 gas log in black on left side. Major unit boundaries are shown as black horizontal lines, estimated location of previous water injection fracture is shown as vertical blue line ($x=45\text{ft}$), estimated location of the CO_2 injection fracture is shown as a vertical green line ($x=60\text{ft}$), perforation intervals for CO_2 injection are shown as magenta dots, and the location of a fault zone is shown as a red diagonal line.

Work Next Quarter

A numerical model study of the Frio Brine Pilot Project site will be conducted. It will be based on flow simulations done using the code TOUGH2. The hydrologic parameters of the flow simulation model will be converted to geophysical parameters based on constitutive relations developed from well logs. Several time steps during the CO_2 sequestration process will be considered, with the goal of determining which geophysical methods are best suited for monitoring the placement of the CO_2 plume. The geophysical techniques considered will include seismic (both surface and borehole-based), electromagnetic, and gravity surveys.

Subtask B-2: Field Data Acquisition for CO Monitoring Using Geophysical Methods

Goals

To demonstrate (through field testing) the applicability of single-well, crosswell, surface-to-borehole seismic, crosswell electromagnetic (EM), and electrical-resistance tomography (ERT) methods for subsurface imaging of CO_2 .

Previous Main Achievements

- The first test of the joint application of crosswell seismic and crosswell electromagnetic measurements for CO_2 monitoring was completed.

Accomplishments This Quarter

- LLNL completed processing and initial interpretation of baseline surveys at ChevronTexaco's Vacuum Field.
- LLNL completed field design for subsequent "time-lapse" survey.

Progress This Quarter

Processing and interpretation of the baseline field surveys at ChevronTexaco's Vacuum Field were completed. Initial results were presented at the January GEO-SEQ Advisory Committee meeting. A report was prepared, detailing the surveys themselves and describing the initial results of the baseline surveys. What follows are excerpts from this report.

The overall purpose of the casing surveys is to provide time-dependent maps of changes in the electrical properties resulting from CO₂ stimulation. An important aspect is to minimize disruption to production/stimulation activities by making use of existing infrastructure (casings). Given only vertical casings available in this instance, only lateral changes in the field will be determined. The initial survey will characterize the overall variability across the region. Subsequent surveys will be used to track changes.

Using standard processing, we obtained an image with resistivities ranging from about 2 to 20 ohm-m (Figure 2A). This is at first surprising, because the reservoir properties are generally quite resistive, in the range of hundreds of ohm-m. However, the baseline image reflects the overall resistivity of the formation to current flow over relatively large distances, using nearly 5,000 ft of steel casing for each electrode. The resulting inversion will be different from a high-resolution image using measurements with what are effectively point electrodes. In the previous casing survey, the resistivities in the baseline survey were within one order of magnitude, as are these. However, in the previous case, the actual values were closer to those of the reservoir materials, which were quite conductive.

The initial inversion revealed a zone (in the center of the image) of increased resistivity surrounded by a nearly symmetric donut of lower resistivity. This symmetry is suspect. Upon further inspection of the raw data, there are some indications that this apparent central zone of high resistivity may be related to the difference in surface line length between measurements made using the central well and those made using only peripheral wells. Since our acquisition system was located next to the central well, its connection cable is only a few feet long, compared to the ~700 ft lengths connecting the system to all the other wells. Reprocessing without the data obtained using the central well results in a much smoother image (Figure 2B). Increasing the contrast shows a slight increase in resistivity toward the southeastern and southwestern edges of the survey area (Figure 2D). We are investigating potential natural or operational mechanisms leading to this small lateral variation.

While working on the field surveys, we have also been conducting experiments in the laboratory using physical models in a large water tank. These experiments utilize models with both point electrode arrays and long electrodes. It was discovered that the resulting image for a casing survey can depend on the measurement schedule. The measurement schedule we used in the field at vacuum was not symmetric, which is most likely affecting the fidelity of the reconstructed image; this will be corrected in subsequent data collections. We are doing additional tests to

verify this result. It was also found that the casings themselves affect current flow during measurements. They must be explicitly included in the processing, which is not possible using 2-D codes. Thus, casing surveys require 3-D interpretations.

The purpose of the point-electrode crosshole survey is to enhance our initial understanding of the baseline reservoir properties and to improve our ability to image changes in the formation electrical properties resulting from movement of CO₂ over time. The initial point-electrode crosshole survey helps establish the key reservoir characteristics prior to influence by injected CO₂. Major features providing contrasts in electrical properties may be delineated, including structural features (e.g., lithologic boundaries) or differences in fluid properties (oil versus water in the pore fluids). The coarse electrode spacing and large well separation prevents high resolution, but the overall characteristics of the reservoir should emerge. Subsequent surveys, if obtained, can be used to detect changes in the formation resulting from fluid movement, because the CO₂ and the formation fluid it displaces have very different electrical properties. Such differences, or “time-lapse” images, have proven effective at monitoring fluid movement in a variety of settings, including fluid infiltration, contaminant movement, and steam injection. The point-electrode crosshole surveys will provide higher resolution (both lateral and vertical) than a casing survey will permit, and should reveal the magnitude of the resistivity changes, particularly in the vicinity of the boreholes. These surveys will be useful for comparison with the crosswell electromagnetic imaging results of Electromagnetic Instruments Inc. (EMI). The two methods, while similar, have different sensitivities to the targets of interest. Obtaining complementary data sets will enhance our understanding of the subsurface phenomena and aid in their interpretation.

Initial processing using all data reveals a smeared image, in which high resistivities (several thousand ohm-m) are seen in the center, with lower resistivities (in the tens of ohm-m) toward the two sides (Figure 3). These data appear to have strong inductive coupling effects, largely a result of the measurement configuration. The inductive coupling here is so large that it appears to swamp whatever signal exists. Next, the data was reprocessed using both 2-D and 3-D codes with adjacent dipoles only to mitigate the inductive coupling (Figure 3), center and bottom images). With the larger dipole separation measurements removed, a more consistent image emerges. The overall magnitude of the resistivities drops to the hundred-ohms-per-meter range. There is some evidence of a structure in which two features extend from the left edge of the image across the image plane toward the center. A single resistive feature of greater thickness appears to extend from the right side toward the center. These features roughly correlate with zones of lower porosity, as evidenced by porosity logs obtained in the two bordering wells. Because of the aspect ratio of the field survey, we expect resolution to be diminished toward the center of the image plane.

Based on field experience and the initial results of the baseline surveys, the design for the first time-lapse data collection has been developed. These surveys are planned for late spring of 2002.

Work Next Quarter

With the arrival of the FY02 funds, we will schedule the first time-lapse data collection for comparison with the baseline surveys. These field surveys will implement improvements to the field procedures developed since obtaining the baseline surveys.

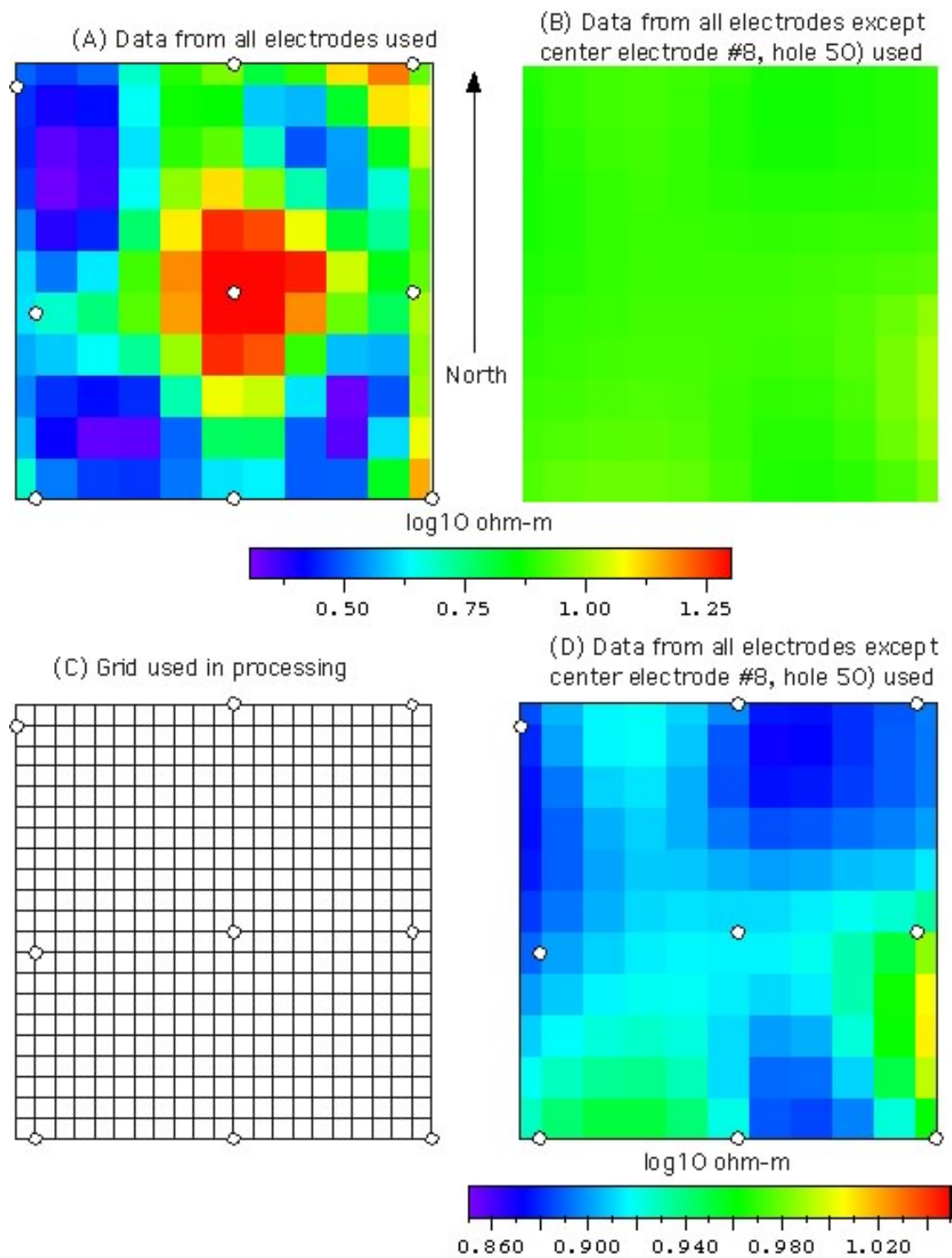


Figure 2. Vacuum field-initial (baseline) casing survey results

Vacuum point electrode results

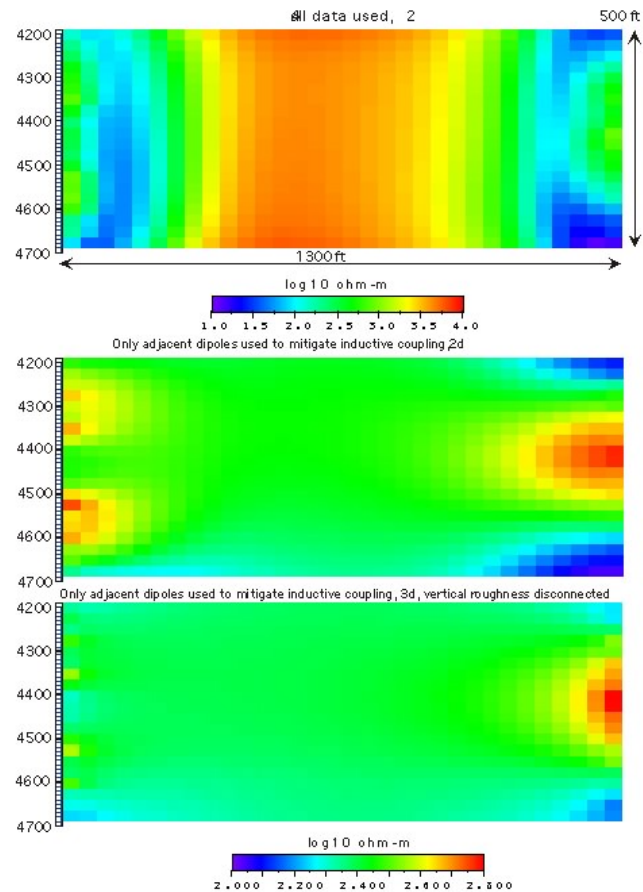


Figure 3. Vacuum field point-electrode results; initial processing. Top, all data used. Center, only adjacent dipoles used to mitigate inductive coupling, 2-D processing. Bottom, only adjacent dipoles used to mitigate inductive coupling, 3-D processing with vertical roughness disconnected.

Subtask B-3: Application of Natural and Introduced Tracers for Optimizing Value-Added Sequestration Technologies

Goals

To provide methods that utilize the power of natural and introduced tracers to decipher the fate and transport of CO₂ injected into the subsurface. The resulting data will be used to calibrate and validate predictive models used for (1) estimating CO₂ residence time, reservoir storage capacity, and storage mechanisms; (2) testing injection scenarios for process optimization; and (3) assessing the potential leakage of CO₂ from the reservoir.

Previous Main Achievements

- Laboratory isotopic-partitioning experiments and mass-balance isotopic-reaction calculations have been done to assess carbon- and oxygen-isotope change (focused on the influence of sorption) as CO₂ reacts with potential reservoir phases.

Accomplishments This Quarter

- Stable isotope measurements of carbon in gases sampled from wells in the Lost Hills area indicate that the injected CO₂ carbon isotope signal was extensively modified during migration through the system subsequent to the second main CO₂ injection episode.
- CO₂ adsorption-desorption measurements have been made on Lost Hills core.

Progress This Quarter

Gas-chromatograph, combustion-isotope-ratio mass spectrometry (GC-C-IRMS) was used to characterize the isotopic and gas chemistry of gases from the Chevron Lost Hills, California system (Figure 4). Carbon and oxygen isotopes were measured in the injection CO₂ (sampled 8/11/00), CO₂ from pre-injection “reservoir” gases (wells 11-8D, 12-8D, and 12-7 sampled 8/11/00), and the return CO₂ sampled in wells 11-8D (sampled 1/4/01; 12/20/01), 12-8D (sampled 12/6/00; 12/20/01), 12-7 (sampled 12/6/00; 12/20/01), 11-7B (sampled 12/20/01), 11-9J (sampled 12/20/01), and 12-8C (sampled 12/20/01). Carbon isotopes have also been measured in C₁-C₆ hydrocarbon gases. The initial injection CO₂ had a $\delta^{13}\text{C}$ (PDB) value of $-30. \text{‰}$ and a $\delta^{18}\text{O}$ (VSMOW) value of -1.12‰ . Gases sampled prior to injection were dominated by CH₄ with lesser amounts of CO₂ and subordinate amounts of C₂-C₆. The $\delta^{13}\text{C}$ (PDB) values for CH₄ in pre-injection and all return gases were very similar, ranging from -36 to -42‰ , with an average of -40.4‰ ($\pm 1.5 \text{‰}$ 1 σ).

The $\delta^{13}\text{C}$ (PDB) values for pre-injection CO₂ ranged from 15.6 to 18.5‰ , whereas the return CO₂ gases from the first sampling effort (12/6/00 and 1/4/01) exhibited a narrow range of values, -27.5 to -29.9‰ . Chemically, return gases from this first sampling effort were very rich in CO₂ and clearly have carbon-isotope values very close to the injection CO₂. Interestingly, the percentages of injection CO₂ estimated from the isotopic data (using -30.1‰ as the injectate end member and 16.8 as the average “reservoir” gas end member) do not agree exactly with similar estimates based on gas chemistry (see Figure 4). In all cases for this first sampling effort, the isotopic mixing model overestimates the amount of injectate CO₂ compared to the gas chemistry model by 6 to 14%. Assuming that the gas chemistry is a better measure of mixing, this means the isotopic values are somewhat more negative (by a few per mil) than simple binary mixing would predict. Pathways that might explain this include (1) loss of CO₂ to an aqueous phase, and/or (2) oxidation of hydrocarbons (CH₄, oil) to CO₂ either inorganically or microbially. The minor differences in predicted mixing percentages based on the isotope and chemical models indicate that these exchange mechanisms made only a minor contribution to the overall carbon isotope budget in the Lost Hills gases immediately after the first main CO₂ injection episode (terminated due to sanding).

This is not true, however, for the gases sampled from all wells on 12/20/01 (see **Figure 4**). Gas chemistries indicate that the amount of injectate CO₂ was less dominant than the previous sampling at the end of 2000. The data show a clear trend on the ternary plot of CO₂-CH₄- Σ C₂-C₆, where samples collected on 12/20/01 fall on a line connecting the “reservoir” gases with gases collected at the end of 2000. Gases with the most amount of injectate CO₂ include those of

wells 11-9J, 12-8C, and 12-7 with $\delta^{13}\text{C}$ values of -20.5 , -19.2 and -17.7‰ , respectively. The remaining wells (11-8D, 12-8D, and 11-7B) have $\delta^{13}\text{C}$ values of -16 , -10.3 and -1.9‰ , respectively. Using the same kinds of simple isotopic and chemical-mixing models for these results indicates that the isotopic model overestimates the percentage of injectate CO_2 by 8 to 20%. CO_2 injected since the sanding problem of 12/00 was carried out as two distinct pulses, one lasting from March to early May 2001, and a second lasting from September to November 2001 (personal comm., Mike Morea, Chevron). Interspersed between these two CO_2 injection pulses was a period of water injection, which was also continued after the last CO_2 pulse in December 2001. The isotopic and chemical data indicate that this complex injection did not lead to a greater influx of CO_2 to the return wells, and in fact seems to indicate that the CO_2 may have had sufficient time to interact more extensively with water and/or hydrocarbons in the reservoir.

The $\delta^{18}\text{O}$ compositions of the pre-injection CO_2 ranged from about 16 to 24‰ (average $\sim 20.9\text{‰}$), whereas the return CO_2 gases from the first sampling effort were somewhat more enriched, ranging from approximately 29 to 34 ‰. Since these samples are dominated by injectate CO_2 (78-90%), this constitutes an approximate $\sim 30\text{‰}$ increase in $\delta^{18}\text{O}$ from the injection value of -1.1‰ . Simple mixing of an isotopically light injectate and the heavy “reservoir” CO_2 cannot explain the even heavier $\delta^{18}\text{O}$ values measured in the three return wells. It is likely that the enrichment in ^{18}O results from kinetically fast exchange of CO_2 with water encountered during migration. The oxygen-isotope fractionation between CO_2 and water is $\sim 37\text{‰}$ at 45°C (a reasonable estimate of the subsurface reservoir temperature), so applying this number to the oxygen values measured for the return CO_2 yields $\delta^{18}\text{O}$ values for water of between -3 and $- \text{‰}$. These values are generally consistent with numbers reported for groundwaters in this part of California. The interaction of CO_2 with the water in the reservoir is also consistent with the carbon-isotope data that suggest possible loss of CO_2 to the aqueous phase as one mechanism to produce isotopic values somewhat more negative than the chemical mixing models predict.

CO_2 adsorption-desorption isotherms were measured at 0 and 17°C for Lost Hills core #4 (1706 ft), using the Quantachrome Autosorb I surface area analyzer (Figure 5). The Lost Hills sample was outgassed at 100°C for several hours. A comparison with previous measurements on N_2 adsorption-desorption indicate that CO_2 adsorbs far less than N_2 , as expected because of its great molecular diameter. Relative to montmorillonite, reported on in the last GEO-SEQ quarterly report, the Lost Hills sample adsorbs roughly five times more CO_2 per unit area (m^2). In both cases, CO_2 exhibits concave upwards adsorption trends for plots of cc/m^2 (y-axis) plotted versus log pressure (x-axis). The magnitude of adsorption and the shape sorption curves are typical for meso- and macroporous solids. Interestingly, the typical temperature dependency—i.e., more adsorption at lower temperature—is not always maintained throughout the trend. In the case of Lost Hills, slightly greater adsorption is observed at low values of P/P_0 (where $P/P_0 = 1$ when $\text{PCO}_2 = 1 \text{ atm}$) at 17°C compared to 0°C . Our isotope-partitioning experiments indicated somewhat more carbon-and oxygen-isotope exchange at higher temperatures for Lost Hills core at the lower pressures, consistent with these new sorption results.

Work Next Quarter

Efforts will focus on four main areas:

1. Continue chemical and isotopic assessment of the next batch of gases sampled at Lost Hills, California.
2. Complete CO₂ sorption-desorption experiments, using Argonne Premium coals as well as Lost Hills core and mineral end-members, quartz, calcite, and Ottawa sand.
3. Continue a modeling effort using Geochemist's Workbench to assess the magnitude of carbon and oxygen-isotope partitioning during gas-brine-mineral reactions relevant to subsurface aquifer formation conditions.
4. Complete construction of flow-through column apparatus and laboratory testing of the applied tracers using the Ottawa sand.

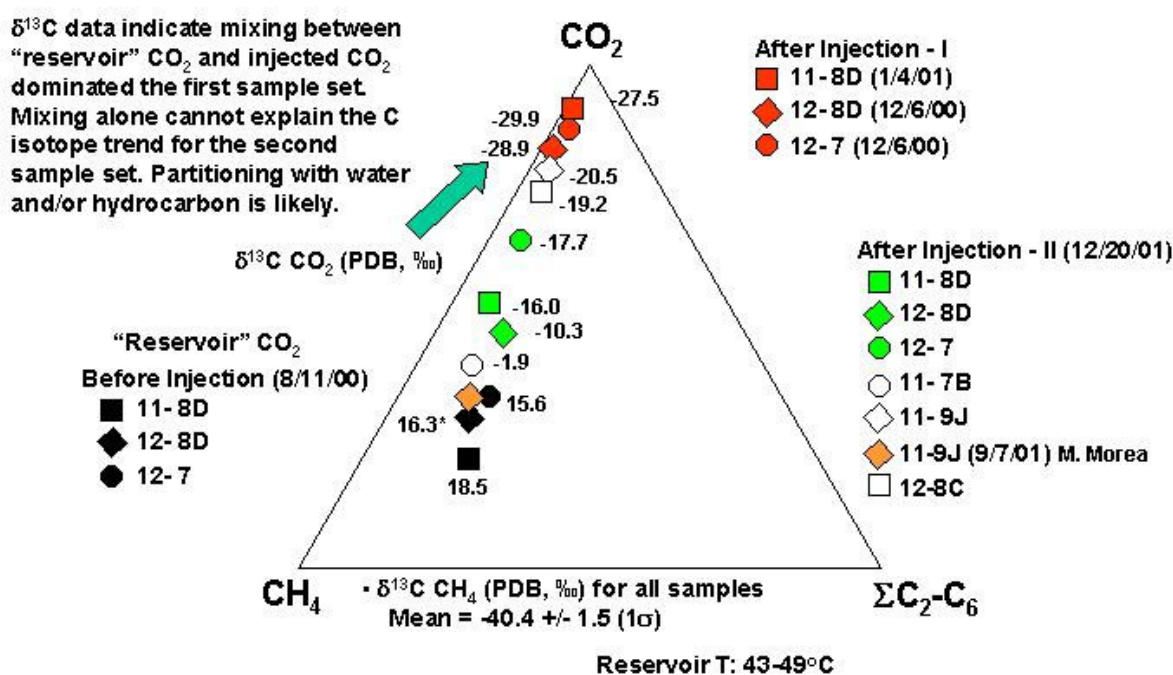


Figure 4. Chemical and carbon isotope data for wells sampled at Lost Hills, California. The injection CO₂ had a δ¹³C value of -30.1‰ and δ¹⁸O value of -1.12‰.

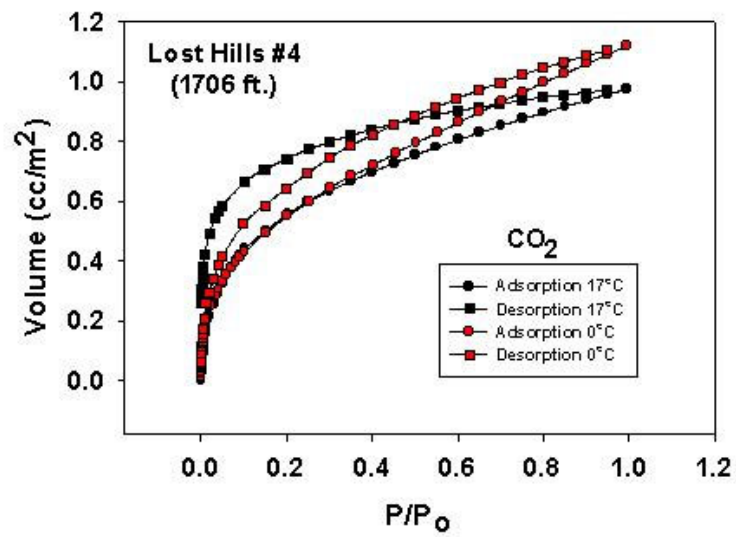


Figure 5. CO₂ adsorption-desorption isotherms for the Lost Hills core #4 obtained at 0 and 17°C

Task C: Enhance and Compare Simulation Models

Subtask C-1: Enhancement of Numerical Simulators for Greenhouse Gas Sequestration in Deep, Unmineable Coal Seams

Goals

To improve simulation models for capacity and performance assessment of CO₂ sequestration in deep, unmineable coal seams.

Previous Main Achievements

- Reservoir simulator-code-comparison studies are underway, providing a mechanism for establishing current capabilities, needs for improvement, and confidence in simulation models.

Accomplishments This Quarter

- Model comparison for the first two sets of simple numerical-simulation problems has been completed, as well as the preparation of two sets of more complex problems.
- Field data obtained from a single-well, micro-pilot test with pure CO₂ injection conducted by the Alberta Research Council (ARC) at the Fenn Big Valley site, Alberta, Canada, has been released to participants for history matching (i.e., Problem Set 5).

Progress This Quarter

Model comparison for the first two sets of simple numerical simulation problems has been completed: Problem Set 1 is a single-well CO₂ injection/production test, and Problem Set 2 is a 5-spot CO₂ injection/production process. The numerical models being tested are CMG's GEM, GeoQuest's ECLIPSE, BP's GCOMP, TNO/CSIRO's SIMEDII and ARI's COMET2. After frequent communications with the participants, it was found that the discrepancy between preliminary results is mainly a result of input errors. In general, there is very good agreement between the final results from different models, as shown in Figures 6 and 7. The good agreement between models is anticipated because of the simplicity of the problems. It is believed that baseline simulation runs have been established for the participating models, which will be tested using the more complex problem sets. Differences in numerical prediction may result from a variety of reasons: (1) handling of the dual-porosity approach in the models; (2) handling of wells (e.g., _ well in 5-spot pattern); and (3) selection of numerical control parameters.

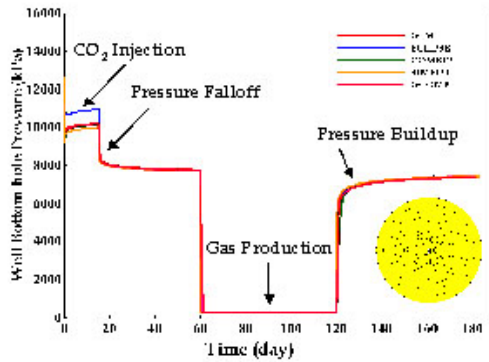


Figure 6. Problem Set 1
Well bottom-hole pressure

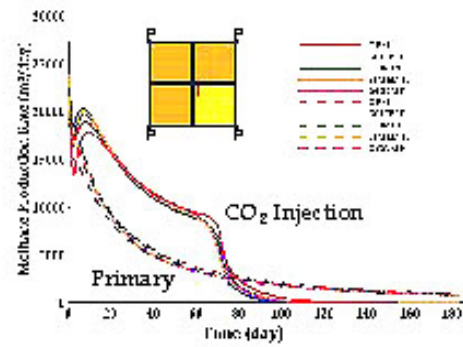


Figure 7. Problem Set 2
Methane production rate

A paper that summarizes the comparison results and describes the current development of the CBM numerical models has been accepted for presentation and publication at the SPE/CERI Gas Technology Symposium (GTS) 2002 (Calgary, Alberta, Canada, April 30–May 2, 2002).

Preparation of two sets of more complex numerical simulation problems has been completed: Problem Set 3 enhances Problem Set 2 by taking into account the effect of gas desorption time (or gas diffusion) between the coal matrix and the natural fracture system; and Problem Set 4 enhances Problem Set 2 by taking into account the effect of natural fracture permeability as a function of natural fracture pressure. Posting of the problem sets on the ARC's password-protected website (<http://www.arc.ab.ca/extranet/ecbm/> (user name: ECBM and password: coal2)) is underway. Preliminary results from CMG's GEM for Problem Set 3 and BP's GCOMP for Problem Set 4 are shown in Figures 8 and 9, respectively.

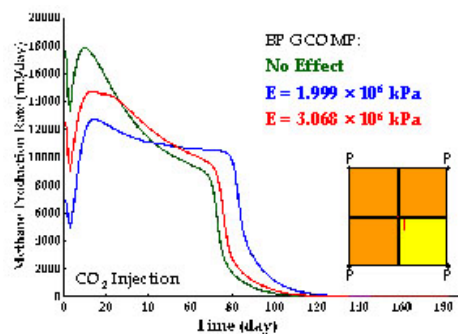


Figure 8. Problem Set 3
Methane production rate
(CMG's GEM)

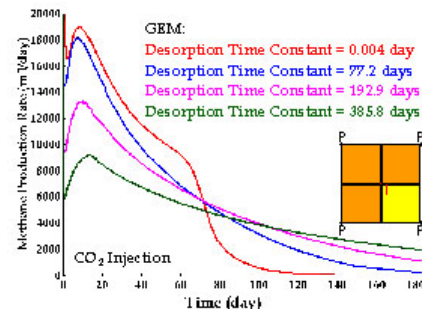


Figure 9. Problem Set 4
Methane production rate
(BP's GCOMP)

Institute Francais du Petrole (IFP, France), Imperial College (U.K.), Akita University (Japan), and Berkeley Lab are potential participants for the model comparison study, in addition to the aforementioned five participants.

Field data obtained from a single well micro-pilot test with pure CO₂ injection conducted by the Alberta Research Council (ARC) at the Fenn-Big Valley site, Alberta, Canada, has been released to TNO and BP for history matching using the models SIMED II and GCOMP, respectively. A confidential agreement has been signed by ARI, and the field data will be released soon to ARI for history matching using the model COMET2.

Work Next Quarter

ARC will organize GEO-SEQ Project, Second Workshop on “Numerical Modeling of Enhanced Coalbed Methane (ECBM) Recovery” in Houston, Texas, March 13, 2002. There are 20 confirmed participants: Rick Chalaturnyk (U. of Alberta, Canada), Steve Talman (U. of Alberta, Canada), Marc Bustin (U. of British Columbia, Canada), Sevkett Durucan (Imperial College, U.K.), Ji Quan Shi (Imperial College, U.K.), George Moridis (Berkeley Lab, U.S.A.), Bill Gunter (ARC, Canada), David Law (ARC, Canada), Scott Reeves (ARI, U.S.A.), Larry Pekot (ARI, U.S.A.), Jeff Levine (CDX, U.S.A.), Peter Sammon (CMG, Canada), Jim Erdle (CMG, U.S.A.), Xavier Chio (CSIRO, Australia), Jim Flynn (GeoQuest, U.S.A.), Charlie Mones (WRI, U.S.A.), John Seidle (Sprouse, U.S.A.), Keith Greaves (TerraTek, U.S.A.), Matt Mavor (Tesseract, U.S.A.) and Bert van der Meer (TNO, The Netherlands). The goal is to discuss the model comparison results to date, the future more-complex problem sets, ECBM mechanisms that are and are not in the existing numerical models (and their importance), how to represent these mechanisms correctly numerically, and the path forward.

ARC investigators will attend COAL-SEQ Forum in Houston, Texas, March 14–15, 2002 to give a presentation entitled “GEO-SEQ Project, Numerical Model Comparison Study for Greenhouse Gas Sequestration in Coalbeds”. ARC will also post Problem Sets 3 and 4 on its website: <http://www.arc.ab.ca/extranet/ecbm/>, as well as document numerical results for those two problem sets. Finally, ARC will initiate testing of Problem Sets 1 and 2 with flue gas injection.

Subtask C-2: Intercomparison of Reservoir Simulation Models for Oil, Gas, and Brine Formulations

Goals

To stimulate the development of models for predicting, optimizing, and verifying CO₂ sequestration in oil, gas, and brine formations. The approach involves: (1) developing a set of benchmark problems; (2) soliciting and obtaining solutions for these problems; (3) holding workshops of industrial, academic, and laboratory researchers; and (4) publishing results.

Previous Main Achievements

- A first workshop on the code intercomparison project was held at Berkeley Lab on October 29-30, 2001, with the first modeling results by different groups showing reasonable agreement for most problems.

Accomplishments This Quarter

- Simulation results for most of the intercomparison test problems were generated in accordance with the reporting requirements that had been agreed upon at the October 2001 workshop held at Berkeley Lab.

- First results were received from other groups.
- An abstract on the code intercomparison work was submitted to the GHGT-6 meeting (Kyoto, Japan, October 2002).

Progress This Quarter

Most of the intercomparison problems were rerun to generate the specific output data that had been agreed upon at the October 2001 workshop at Berkeley Lab. We maintained contact with the other groups working on the problems and received first results. An abstract summarizing objectives and (expected) results of the code intercomparison study was prepared and submitted to the GHGT-6 meeting in Japan.

Work Next Quarter

We will plot and compare results from the different groups, and will then contact them to discuss whatever discrepancies may turn up. We will begin preparing a narrative description and comparison of results.

Task D: Improve the Methodology and Information for Capacity Assessment

Goals

To improve the methodology and information available for assessing the capacity of oil, gas, brine, and unmineable coal formations; and to provide realistic and quantitative data for construction of computer simulations that will provide more reliable sequestration-capacity estimates.

Previous Main Achievements

- A new definition of formation capacity, incorporating intrinsic rock capacity, geometric capacity, formation heterogeneity, and rock porosity, was developed for use in assessing sequestration capacity.
- An assessment of CO₂ sequestration capacity of California was carried out.
- Factors affecting sequestration capacity of the Frio formation in Texas have been evaluated.
- The Texas Gulf Coast was targeted as an area from which a realistic data set could be generated for use in simulating brine-formation capacity.
- Location and identifying information were compiled for large industrial CO₂ emitters, and geologic data for the Frio and Oakville reservoirs were compiled.
- A realistic scenario for CO₂ injection into a brine formation was then designed for a site near Baytown, Texas; its brine-formation capacity for CO₂ storage was assessed based on numerical-simulation studies.

Accomplishments This Quarter

- DOE has selected the Bureau of Economic Geology (BEG) GEO-SEQ proposed pilot project entitled "Optimal Geological Environments for Carbon Dioxide Disposal in Brine Formations in the United States—Pilot Experiment in the Frio Formation, Houston Area."

- Logistical and scientific organizational tasks, including coordination of GEO-SEQ activities to be performed at the Frio site have begun, as well as the geologic characterization of the injection target needed to perform support modeling studies.
- Simulation studies using the representative model of the shallow Frio formation have further elucidated the relationship between geologic heterogeneity, operational controls (such as well completion intervals), and capacity factors.
- The fate of CO₂ in immiscible and dissolved phases after injection ceases has been investigated.

Progress This Quarter

Several variations on the shallow Frio (1,000 m x 1,000 m x 100 m thick) model described in previous GEO-SEQ quarterly reports, were simulated to examine the effects of heterogeneity on CO₂ sequestration for a 20-year injection period, during which 750,000 English tons of CO₂ were injected per year, followed by a 60-year recovery period. The base-case model is described by Hovorka et al. (2001) and is in earlier GEO-SEQ quarterly reports.

In the first three cases, an injection well penetrates the lower half of the formation. We believe that this makes the most sense for a system with strong buoyancy flow.

1. Shallow Frio (base case)—fluvial heterogeneity representative of the shallow Frio.
2. Uniform sand—homogeneous medium with properties of the sand channel facies in the shallow Frio model.
3. Sealed shale—like the shallow Frio model, except the vertical permeability for all facies within shaly depositional settings is very low (equal to the vertical permeability of the shale facies). This has the effect of making the shale layers continuous sealing layers.
4. Sealed shale, fully penetrating injection well—for the sealed shale case, the gas saturation distribution indicates that a lower-half-penetration injection well is not necessarily a good idea, so a final case considers a full-penetration injection well.

Figures 10–13 show the spatial distributions of supercritical CO₂ in an immiscible gas-like phase (S_g) and CO₂ dissolved in the aqueous phase ($S_i X_i^{CO_2} \rho_i / \rho_{CO_2}$) at three times: after 1 year of injection, when the outer boundary of the model is generally just beginning to be felt; after 20 years of injection, at the end of the injection period; and after 40 years of subsequent recovery, during which no injection occurs. The capacity factor is also shown as a function of time for each case. The capacity factor has been defined to quantify the effectiveness of a subsurface volume to sequester CO₂ (see Doughty et al., 2001, and previous quarterly reports for details). The total capacity factor C represents the volumetric fraction of the subsurface containing CO₂. C can be divided into C_g , the fraction containing gas-phase CO₂, and C_i , the fraction containing CO₂ dissolved in the aqueous phase ($C = C_g + C_i$).

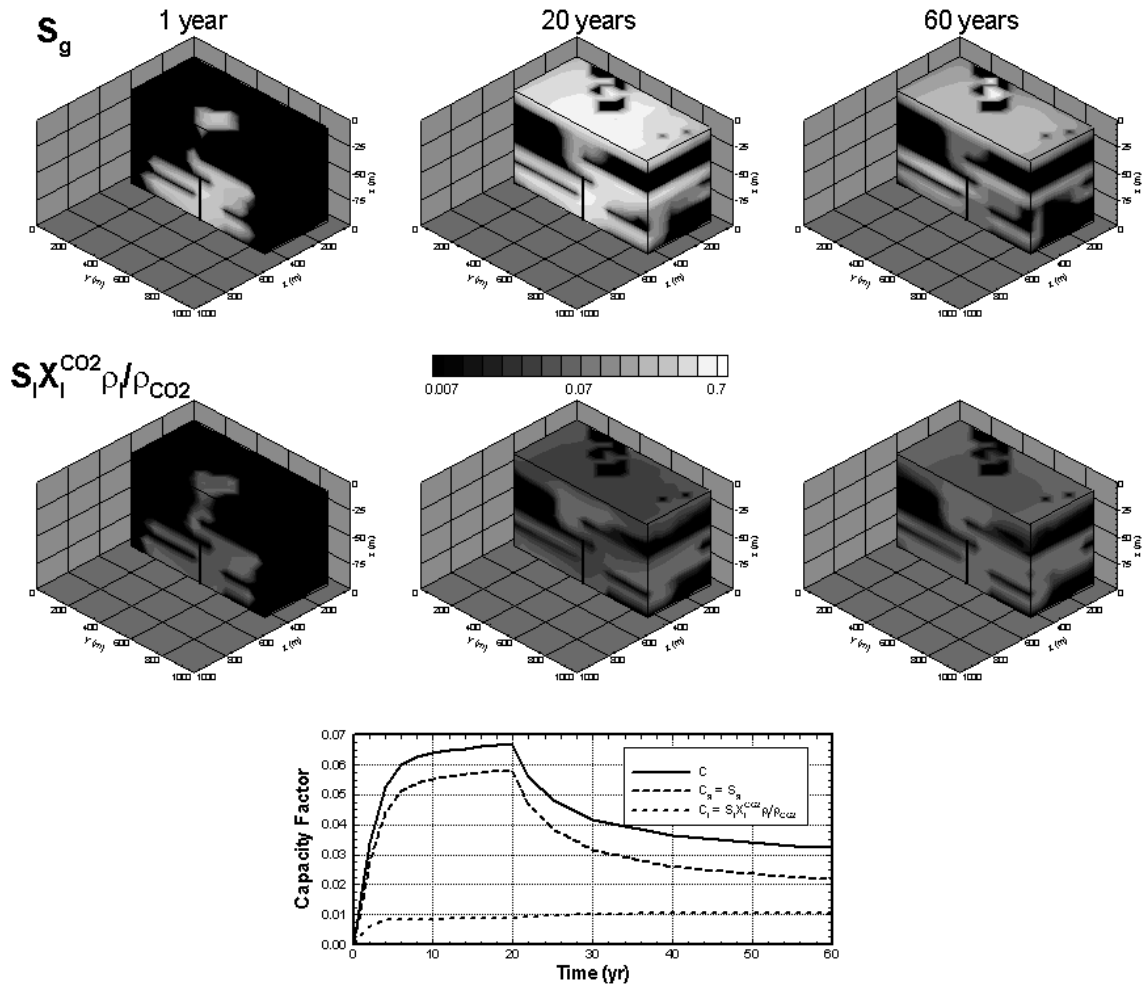


Figure 10. Shallow Frio, base case (see text)

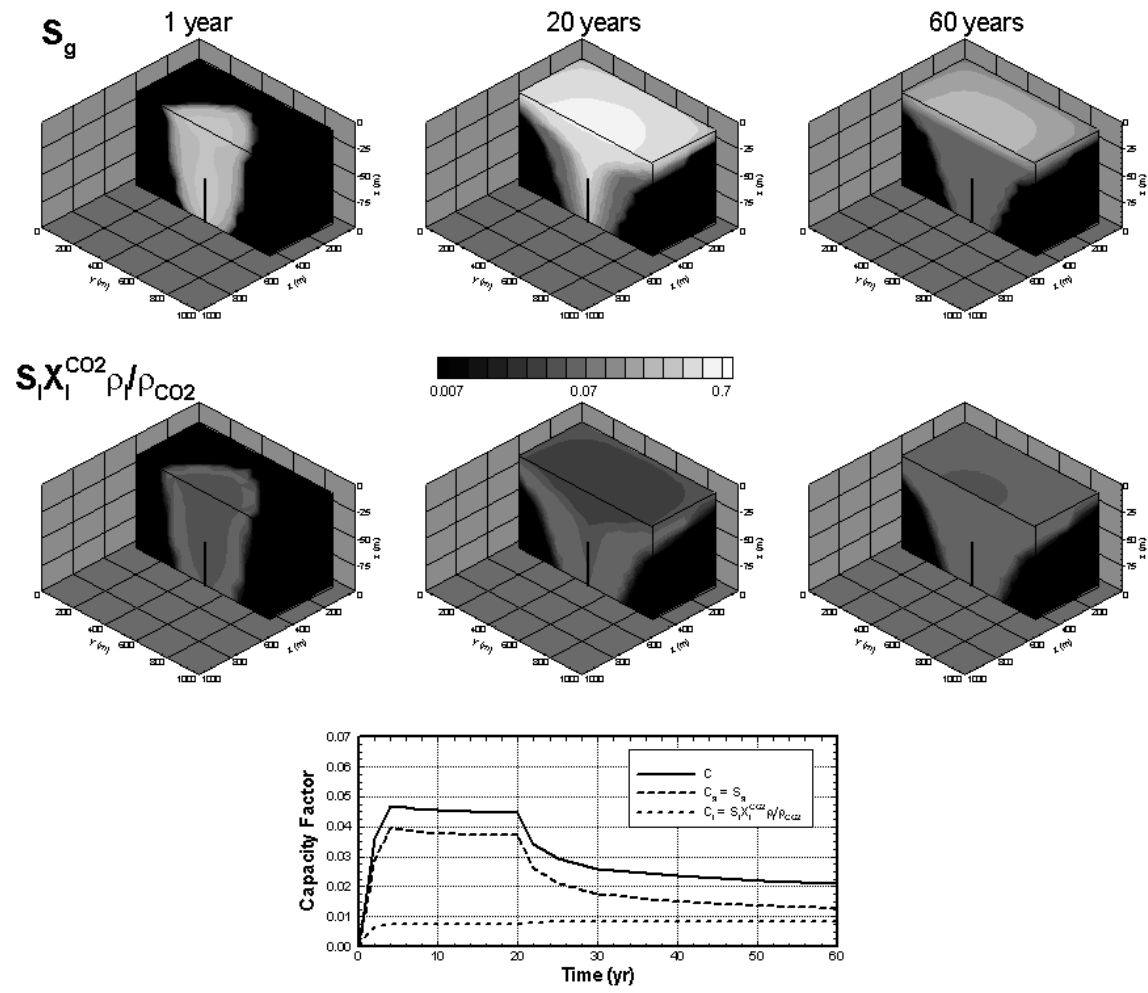


Figure 11. Uniform sand (see text)

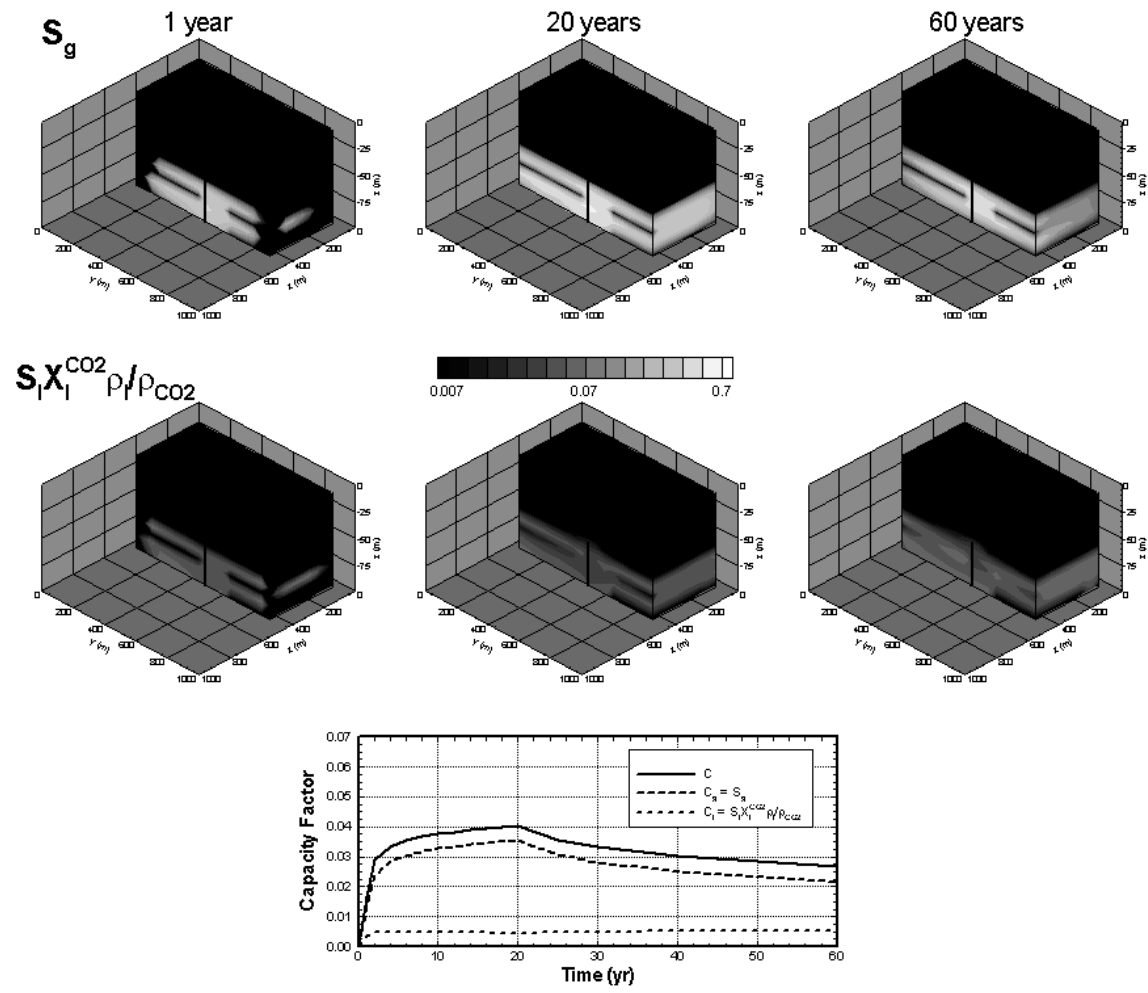


Figure 12. Sealed shale (see text)

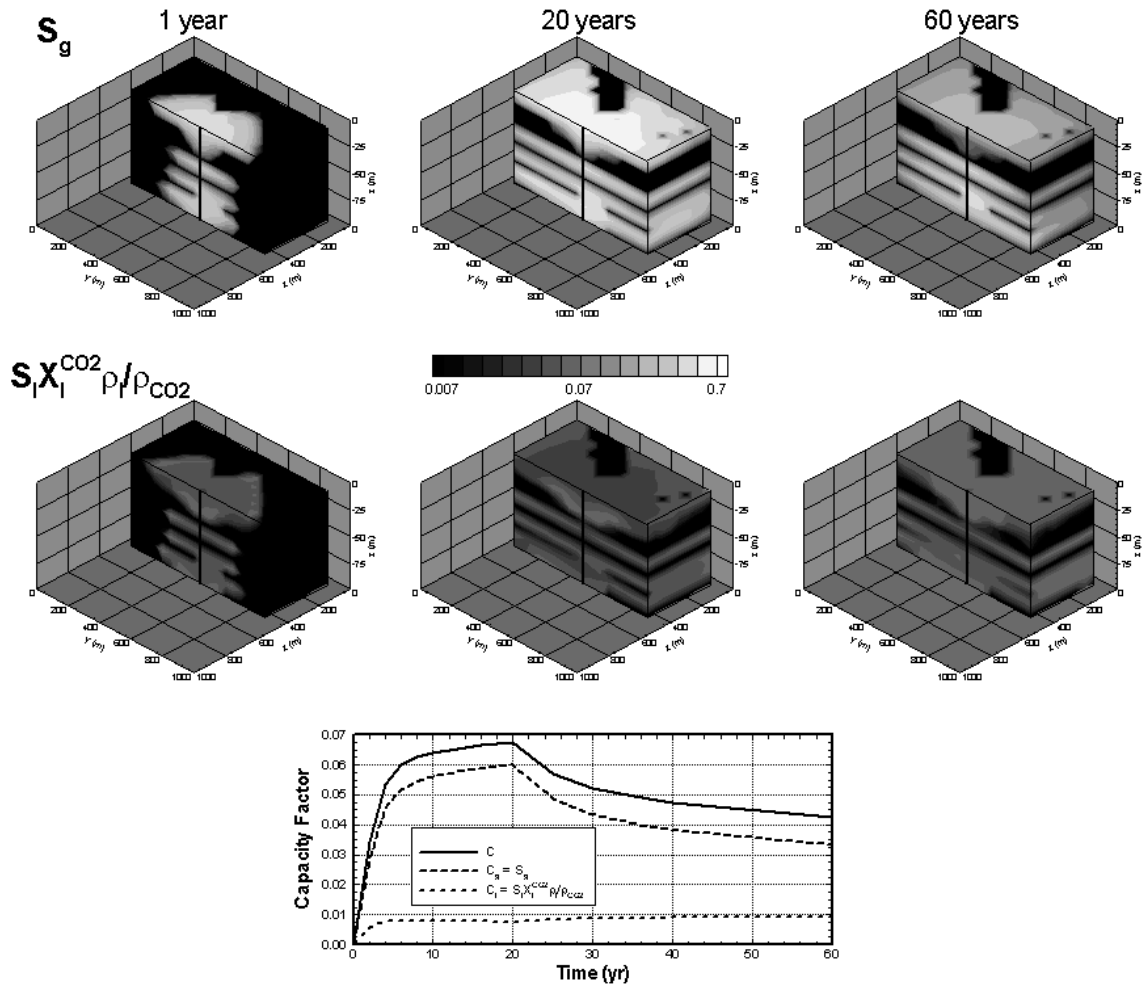


Figure 13. Sealed shale, fully penetrating injection well (see text)

It is clear that the presence and the discontinuous or continuous character of the shale layers has an important effect on the CO₂ distribution. Injected CO₂ avoids the shale layers because their permeability is so much lower than that of the sands. Because the gas-phase CO₂ has a much lower density than the brine (577 kg/m³ versus about 1,000 kg/m³), buoyancy has a strong effect wherever vertical permeability is sufficient to enable flow. Carbon dioxide dissolved in the aqueous phase is not subject to significant buoyancy forces, so it provides a picture of where the gas-phase CO₂ has been.

For all cases, C_g is significantly larger than C_i throughout the injection period. For longer-term sequestration after injection has ended, C_g decreases as buoyancy flow drives CO₂ up and out of the lateral boundaries of the model, whereas C_i continues to increase slowly, ultimately making C_i a significant fraction of C.

Table 1 summarizes some of the features of capacity-factor time variation for the different cases. The time to reach the spill point (i.e., when CO₂ first reaches the outer model boundary) is inversely proportional to the flow-path volume available as CO₂ moves away from the injection interval. A continued increase in capacity occurring after the spill point is reached indicates that additional volumes within the model are filling with CO₂, even after the leading edge of the CO₂ plume has reached the model's boundary. Discontinuous shale layers are particularly effective in enabling buoyancy flow to fill the upper half of the model for the base case with a lower-half penetration injection well. The rate of C_g decline during the recovery period is indicative of how easily gas-phase CO₂ can reach the lateral model boundaries. The sealed shale cases, which severely limit buoyancy flow, provide limited opportunities to find paths to the boundaries, slowing the decline of C_g.

Table 1: Capacity-factor time variations for the different Frio cases studied

Case	Time to Reach Spill Point (Yrs)	Continued Increase in C after Spill Point	Rate of C _g Decline after End of Injection
Lower-half penetra			
1. Shallow Frio	1	Yes	Fast
2. Uniform sand channel	2	No	Fast
3. Sealed shale	0.5	Yes	Slow
Full penetration			
4. Sealed shale	2	Yes	Slow

Accomplishments related to the Frio Brine Pilot Project include reviewing and ranking GEO-SEQ goals that can be accomplished at this site. The review has two goals: (1) identification of the field support needs for GEO-SEQ tasks and (2) developing a matrix for prioritization of goals and the available methods that can be used to accomplish these goals. This review provided input to the request for proposals from prospective field service providers (FSP). The FSP will supply UIC and oilfield CO₂ handling experience and conduct or subcontract field activities required to support the project objectives. The request for proposals has been completed and sent to six qualified companies, with responses due April 16, 2002.

Available data from the operator has been obtained by BEG in digital and paper formats, and geologic characterization is underway. At this time, the data are considered proprietary; however, BEG will develop derived products and make them available to project team members as soon as possible. Major elements included in characterization are (1) analysis of a 3-D seismic volume, including the injection target in the upper Frio Formation; (2) acquisition of wireline log suites and check shots; (3) identification of available core and cuttings, and (4) compilation of existing brine, chemical, and petrographic data.

Work Next Quarter

Berkeley Lab and BEG will complete capacity studies and write a journal article about them. They will also conduct modeling studies in support of the Frio Brine Pilot Project (i.e., pilot CO₂ injection experiment). In addition, the GEO-SEQ team will design a detailed project plan and timeline for the Frio Brine Pilot Project, submitting NEPA checklists and continuing the characterization. BEG will make geologic characterization data available to the project team as quickly as possible. The goal of characterization is to create a single, detailed 3-D geocellular model that can be used as a basis for simulations by team members. The model will incorporate geological structure, stratigraphy, and petrophysical and fluid properties.

References

- Hovorka, S.D., C. Doughty, P.R. Knox, C.T. Green, K. Pruess, and S.M. Benson, 2001, Evaluation of brine-bearing sands of the Frio Formation, upper Texas Gulf Coast for geological sequestration of CO₂, Proceedings, First National Conference on Carbon Sequestration, May 14-17, Washington DC, National Energy Technology Laboratory, Paper 4A.2.
- Doughty, C., K. Pruess, S.M. Benson, S.D. Hovorka, P.R. Knox, and C.T. Green, 2001, Capacity investigation of brine-bearing sands of the Frio Formation for geologic sequestration of CO₂, Proceedings, First National Conference on Carbon Sequestration, May 14-17, Washington DC, National Energy Technology Laboratory, Paper P.32.